

Periodic Mesoporous Organosilica Nanorice

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Abstract A periodic mesoporous organosilica (PMO) with nanorice morphology was successfully synthesized by a template assisted sol–gel method using a chain-type precursor. The PMO is composed of D and T sites in the ratio 1:2. The obtained mesoporous nanorice has a surface area of $753 \text{ m}^2 \text{ g}^{-1}$, one-dimensional channels, and a narrow pore size distribution centered at 4.3 nm. The nanorice particles have a length of ca. 600 nm and width of ca. 200 nm.

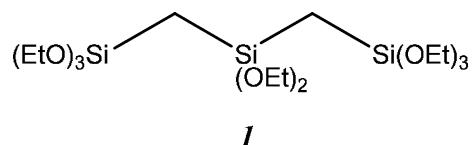
Keywords Nanorice · Mesoporous materials · Periodic mesoporous organosilica

Introduction

Periodic mesoporous organosilicas (PMOs) have emerged as a diverse class of materials with numerous potential applications [1–3]. PMOs are attractive because they have a much higher and uniformly distributed loading of organic groups compared to organosilicas with post-grafted organic groups and organosilicas with terminal organic groups that have to be prepared by co-condensation methods [1–3]. Very little is known about the synthesis of PMO nanoparticles of controlled size and shape [4–7], and to our best knowledge there are no reports about uniform submicron PMO nanoparticles. Size and shape of mesoporous particles have a considerable impact on their potential uses. For example, periodic mesoporous silica nanoparticles of designed shapes have emerged as promising candidates for drug-delivery applications [8]. Generally, it is difficult to

achieve periodic mesoporous particles of uniform anisotropic shape and size, and special techniques are needed to produce them rationally and reproducibly [9–11]. Nanorices have been so far reported for dense nanoparticles, namely, iron oxide [12], organic polymers [13], silver [14], gold [15], and cobalt [16].

Herein, we report about the synthesis of periodic mesoporous organosilica nanorice from a novel chain-type precursor octaethoxy-1,3,5-trisilapentane **1**. In this precursor molecule two Si atoms are bound to one organic bridging group (T site) while one Si is bound to two organic bridging groups (D site). This structural motif DT₂ has not been used so far in PMO chemistry. Thus, the reported PMO has a novel composition and structure.



The nanorice was reproducibly obtained in a standard block copolymer template assisted sol–gel route [17] at room temperature without the need of any special reaction conditions.

Experimental

Materials and Methods

Materials

Triblock copolymers EO₂₀PO₇₀EO₂₀ Pluronic P123 (BASF, USA), octaethoxy-1,3,5-trisilapentane (EtO)₃Si–CH₂–Si(OEt)₂–CH₂–Si(OEt)₃ (Gelest) and NaCl (EM Science) were used as-received without further purification.

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Synthesis of PMO Nanorice

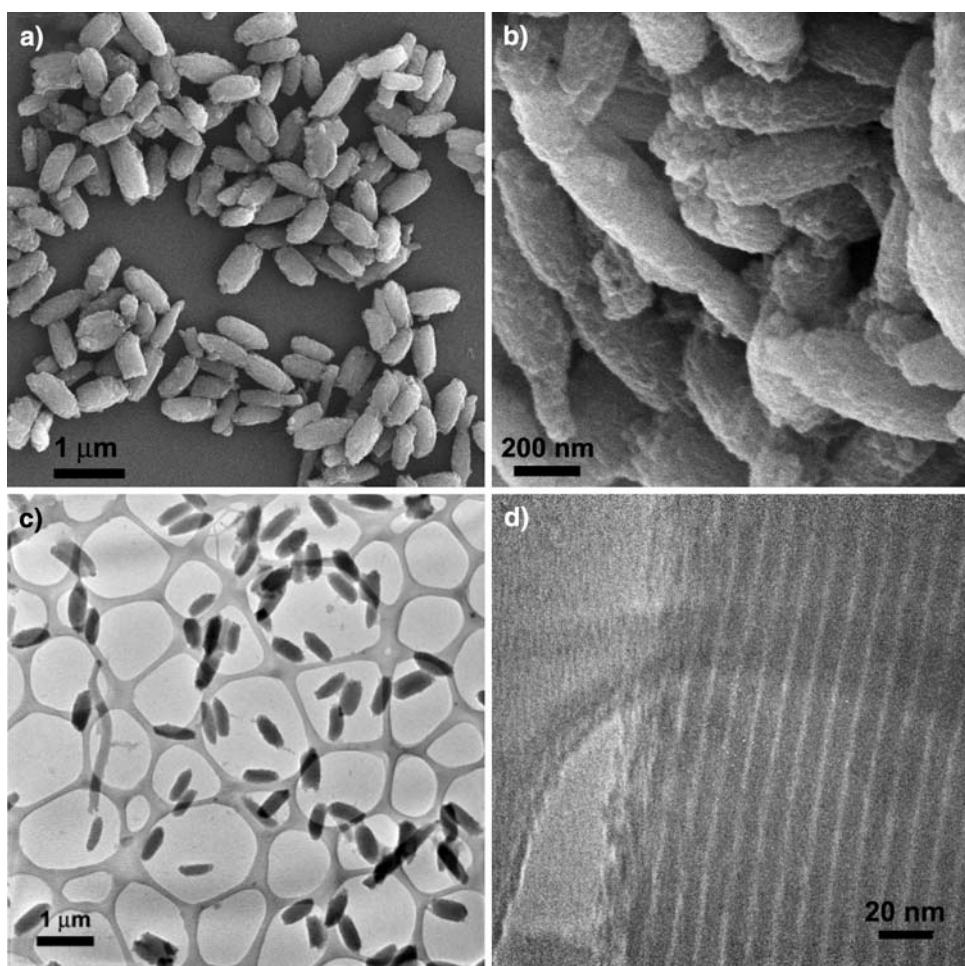
To a mixture of 6 g NaCl, 1.3 g of Pluronic 123, 32.4 mL (33.6 g) of 2 molar HCl and 11.2 mL H₂O, 1.44 g of **1** was added drop wise under vigorous stirring. The mixture was continuously stirred for another 24 h under the formation of a suspension of a white solid. The solid particles were centrifuged off and re-suspended in a mixture of 100 mL acetone and 10 mL 2 molar HCl. This mixture was stirred for another 48 h to extract the template. The extracted particles were centrifuged again and dried at 80 °C for 1 h to yield 443 mg of final product.

Characterization of the Materials

The TEM images were taken on a JEOL JEM-2000 electron microscope operated at 200 kV. Samples for the TEM analysis were prepared by dispersing the particles in acetone and dropping a small volume of it onto a holey carbon film on a copper grid. SEM images of the specimen were taken on a Hitachi S-4300 SEM. SAXS patterns were

obtained using a Rigaku Rotaflex diffractometer with a Cu K_α radiation source ($\lambda = 0.15405$ nm). The N₂ adsorption isotherm was measured at 77 K using an ASAP 2010 (Micromeritics Instrument Corp.). The free space He was determined prior to measuring the N₂ isotherm on a sample that was activated at 150 °C under dynamic vacuum to a vacuum of $<10^{-5}$ Torr. After measuring the free space with He, the sample was again outgassed at 150 °C prior to measuring the N₂ isotherm. The BET surface area was calculated over the pressure range of 0.04–0.1 P/P₀. The ¹³C and ²⁹Si NMR spectra were obtained at 59.616 MHz (silicon-29) or 75.468 MHz (carbon-13) on a General Electric NMR Instruments model GN-300 equipped with a Doty Scientific 7 mm MAS probe. One pulse spectra were measured with a 1.0 μ s pulse length (corresponding to a 20 degree tip angle) and a relaxation delay of 5.0 s (silicon) or 10 s (carbon) for 16,000 to 29,000 acquisitions while spinning at typically 5.0 kHz. Additional spectra (not shown) were acquired to assure quantitative NMR signal intensities. Proton decoupling during the 40 ms acquisition time was performed with a continuous 70 kHz radiofrequency

Fig. 1 **a, b** SEM and **c, d** TEM images of PMO nanorice



field at 300.107 MHz. The time domain signal was conditioned with a Gaussian line-broadening function equivalent to 50 Hz prior to Fourier transformation.

Results and Discussion

The PMO nanorice particles have a narrow size distribution with an aspect ratio of ca. 3:1 (ca. 600 nm length, ca. 200 nm width) as seen by SEM and TEM (Fig. 1). The round ends and the relatively low aspect ratio make the nanorice structure clearly distinguished from nanorod type structures. TEM investigations further reveal a mesostructure with periodic one-dimensional channels with pore sizes of ca. 4 nm and channel wall diameters of ca. 6 nm. The mesochannels are highly aligned and run parallel to the largest particle dimension (Fig. 1d). Small angle powder-X-ray diffraction confirms the formation of a periodic mesostructure (Fig. 2). An intense reflex with an interplanar spacing $d = 10.4$ nm is observed corresponding to a lattice parameter $a = 12$ nm.

^{13}C MAS NMR (Fig. 3a) demonstrates the existence of organic groups in the framework. The signals around 5 ppm can be assigned to the CH_2 groups that bridge the Si tetrahedral centers. The absence of any further signals shows that the material is practically template free. ^{29}Si MAS NMR investigations (Fig. 3b) reveals that practically no Si–C bonds have cleaved during the synthesis and template removal process. The signals observed between –8 and –32 ppm can be assigned to D sites. The signals around –16 ppm represent D_1 sites, while signals around –24 ppm represent D_2 sites at the chain centre. The signals between –39 and –73 ppm can be assigned to T sites at the chain ends. The spectrum indicates the simultaneous presence of T_1 , T_2 , and T_3 sites at –48, –55, and –59 ppm, respectively.

The material shows a classical type IV isotherm with an N_2 hysteresis (Fig. 4a). The multipoint BET analysis reveals an N_2 surface area of $753 \text{ m}^2 \text{ g}^{-1}$. The Gurvich volume of the sample at a P/P_0 of 0.97 was found to be 0.62 cc/g which is higher than the total pore volume from the desorption branch (0.51 cc/g). This phenomenon can be explained by interparticle void filling at high partial pressures. Calculation of the liquid N_2 pore volume at 350 cc/g (the plateau region) using the standard molar volumes for N_2 at 77 K gives a pore volume of 0.54 cc/g which is in good agreement with the total pore volume (0.51 cc/g) obtained from the desorption branch of the isotherm. From the desorption branch BJH analysis reveals a very narrow pore size distribution centered at 4.3 nm (Fig. 4b) which is in good agreement with the TEM data.

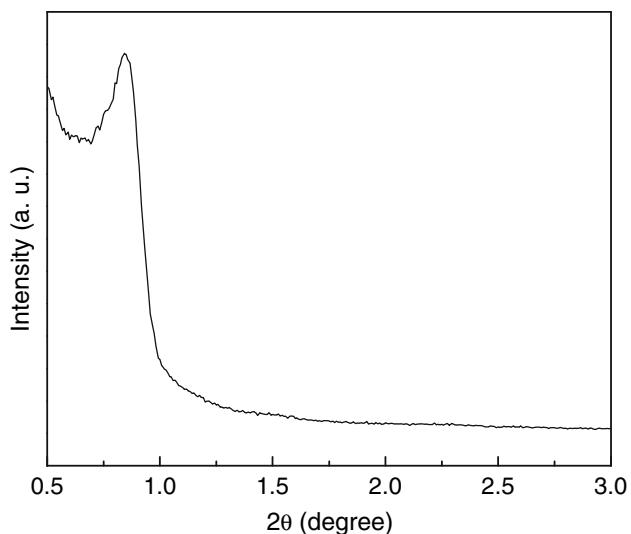


Fig. 2 SAXS pattern of PMO nanorice

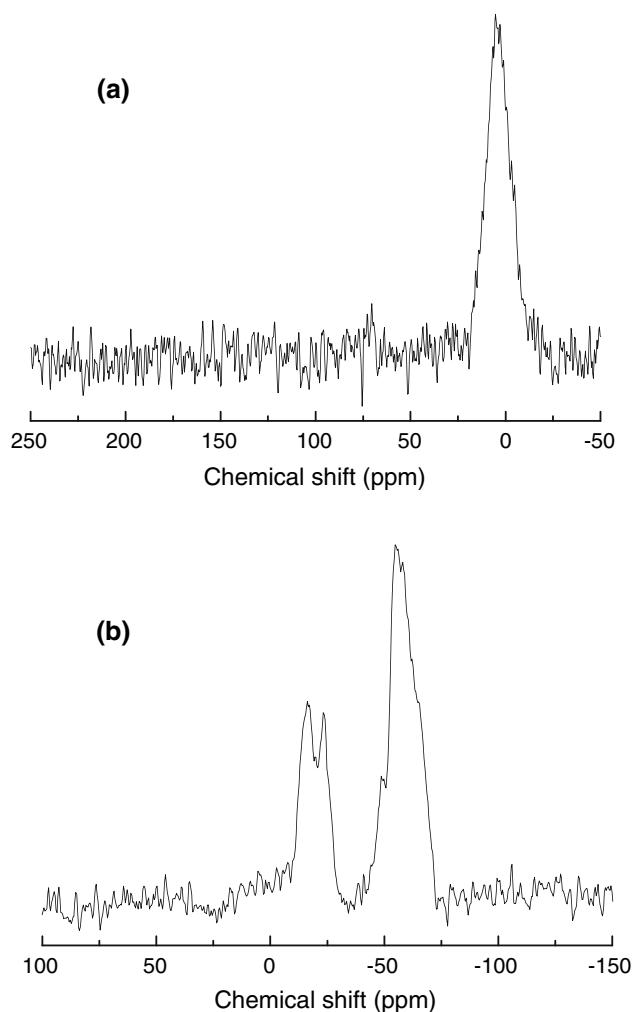


Fig. 3 **a** ^{13}C and **b** ^{29}Si MAS NMR spectra of PMO nanorice

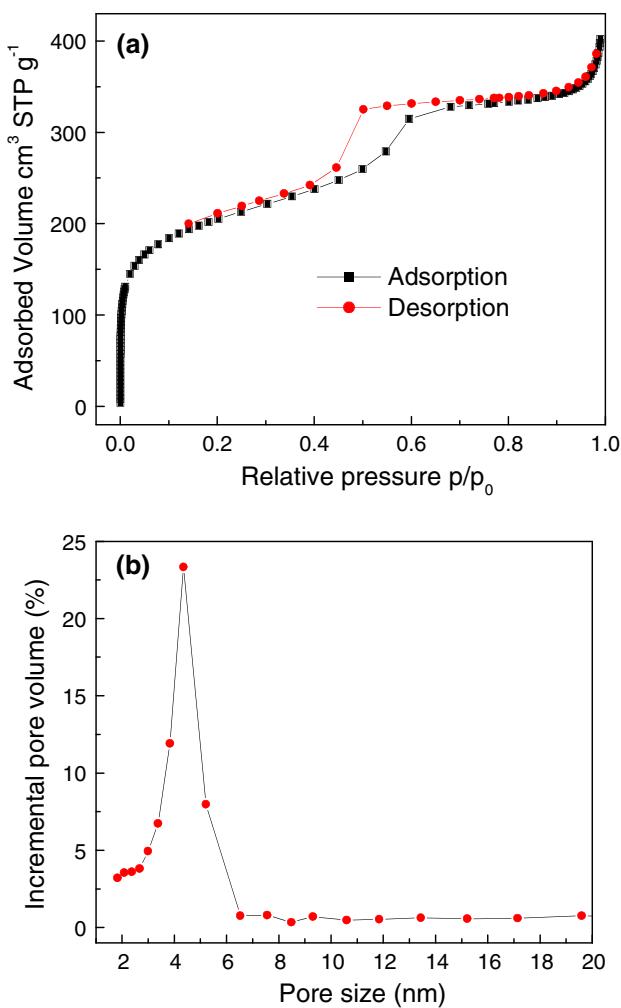


Fig. 4 **a** N₂ sorption isotherm and **b** BJH pore size distribution of PMO nanorice

An interesting fact is that the aspect ratio of the obtained nanorice particles is close to the aspect ratio of the chain-type precursor and its hydrolyzed form (Fig. 5). This suggests that the hydrolyzed precursor may orient in a head-on manner with respect to the cylindrical micelles. Assuming equally fast polycondensation in all dimensions the particle grows anisotropically according to the aspect ratio of the precursor explaining the nanorice shaped particles.

Conclusions

In summary, we have synthesized a PMO with well-defined nanorice morphology. The particles are rather uniform and have a length of 600 nm and a width of 200 nm. A novel chain-type precursor with a DT₂ structural motif was used in the self-assembly process. The nanorice particles could be obtained in a surfactant templated self-assembly process without the need of a novel methodology or any other special aids.

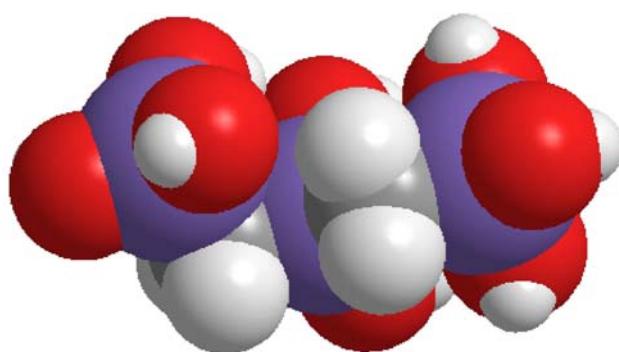


Fig. 5 Space-filling model of the energy-minimized hydrolyzed precursor (OH)₃SiCH₂Si(OH)₂CH₂Si(OH)₃

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